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Application of the GCA-EoS model to the supercritical processing of fatty oil derivatives

Olga Ferreira [a], Eugénia A. Macedo [a,*], Esteban A. Brignole [b]

[a] *LSRE—Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[b] *PLAPIQUI, UNS—CONICET, CC 71, Km 7, Camino La Carrindanga, 8000 Bahía Blanca, Argentina*

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Abstract

The group-contribution with association equation of state (GCA-EoS) is applied to represent high-pressure phase equilibria in mixtures of supercritical gases (carbon dioxide, propane) with fatty oil derivatives, such as mono- and di-glycerides, fatty acids and fatty acid esters.

Association effects in these mixtures are described by a group-contribution approach using three different association groups: the hydroxyl group, the acid group and the ester group.

Satisfactory predictions of vapor–liquid equilibria, liquid–liquid equilibria and γ^{∞} of binary and ternary mixtures of high-molecular weight triacyglycerides and their derivatives with carbon dioxide or propane are obtained.

It is shown that the GCA-EoS is a powerful engineering tool for the design and optimization of extraction and fractionation processes of fatty oil derivatives with supercritical fluids.

Keywords: Fatty oils; Phase equilibria; Thermodynamic modelling; Association; Group-contribution

1. Introduction

The design of extraction, fractionation and purification processes involving fatty oils and their derivatives, using near critical or supercritical fluids as solvents, requires the existence of thermodynamic models that are able to represent these highly complex mixtures that include high-molecular weight triglycerides and their derivatives with low-molecular weight solvents.

Usually, these natural products mixtures are described using cubic equations of state like Peng and Robinson (1976) or Soave (1972). Some authors (Yu, Zou, Bhaskar, Rizvi, & Zollweg, 1993) used the Peng–Robinson EoS with the Panagiotopoulos and Reid mixing rules to correlate vapour–liquid equilibria (VLE) of ternary mixtures of CO_2 + methyl oleate + oleic acid. Two interaction parameters for each pair of components were estimated. Other researchers (Fuente, Fornari, Brignole, & Bottini, 1997) have applied the SRK-EoS with quadratic mixing rules to correlate vapour–liquid and liquid–liquid equilibria (LLE) data for mixtures containing sunflower oil with ethane and propane. In order to predict the appearance of a liquid–liquid split, binary interaction parameters for both the attractive energy parameter and the co-volume were introduced. However, it was not possible to describe quantitatively both VLE and LLE using only one set of parameters for the co-volume, which indicated the limitations of the van der Waals repulsive term to describe these asymmetric mixtures. More recently, the Peng–Robinson EoS

* Corresponding author. Tel.: +351 222041653; fax: +351 222041674.
E-mail address: eamacedo@fe.up.pt (E.A. Macedo).

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